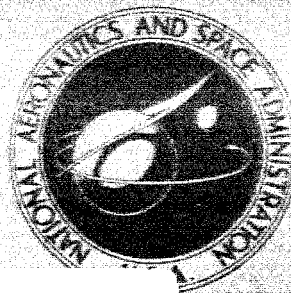


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FOR SEALING METALLIC AND
PLASTIC FILMS FOR USE AT
LIQUID-HYDROGEN TEMPERATURES

by Paul T. Hacker

Lewis Research Center

Cleveland, Ohio

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SUMMARY

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An experimental investigation was conducted to evaluate the ability of 15 different adhesives to provide a hermetic seal in lap joints between thin metallic foils and plastic films in the presence of gaseous and liquid hydrogen. The lap joints were tested in a manner that provided a pressure difference of 20 pounds per square inch through the adhesive bond line but did not subject the joint to any mechanical stresses or loads. Each adhesive was tested at room, liquid-nitrogen (-320°F), and liquid-hydrogen (-423°F) temperatures. The adhesives tested are commercially available and included epoxy-polyamines, nylon-filled epoxies, urethanes, polyesters, and rubber-based adhesives. In general, the most satisfactory adhesives system for sealing aluminum to aluminum, Mylar to Mylar, and Mylar to aluminum at cryogenic temperatures are the epoxies.

INTRODUCTION

The use of liquid hydrogen as a rocket propellant has established a critical need for large, lightweight, well-insulated tank structures. Much effort is being directed toward the development of materials and methods of fabrication that will reduce the weight of rocket propellant tanks and increase the efficiency of the insulation systems. One method of reducing tank weight currently under study at the NASA Lewis Research Center is the use of filament-wound fiber-glass structures. The approach appears promising because the strength to density ratio of fiber-glass composite structures is considerably higher than materials currently used for liquid-hydrogen tanks (approx. three times that of aluminum). Filament-wound fiber-glass structures have been used successfully, to date, in the development of lightweight solid rocket motor cases.

The major problem encountered in using fiber-glass structures for liquid-propellant tanks is their porosity. All filament-wound tanks become porous at some stress level below the burst strength. Therefore, to prevent liquid propellants from escaping through the tank wall, an impervious liner or barrier is required. To retain the weight advantage gained by the use of filament-wound fiberglass, the impervious liners must be lightweight and, therefore, of very thin material. The impervious liners used in

rocket motor cases are composed of elastomers. For the present state of the art, elastomers cannot be used at liquid-hydrogen temperatures because of severe embrittlement and thermal shrinkage problems.

A large selection of metallic foils and plastic films is available for possible use as liner materials, but these materials need to be evaluated for physical properties (permeability, strength, etc.) at cryogenic temperatures and for mechanical compatibility with fiber-glass structures. Metallic foils, in general, are less permeable than plastic films, but they are more susceptible to the development of cracks and pinholes caused by wrinkling and folding during normal handling. A laminate of an impermeable metallic foil and a tough plastic film, such as Mylar, appears more attractive. In most cases a one-piece liner cannot be fabricated; therefore, the material used for the liner must be joined to itself to form a hermetically sealed joint. For these films, both metallic and plastic, adhesive bonding has been the only practical method of joining; however, very little specific information is currently available on the physical properties of commercial adhesives at cryogenic temperatures.

Several studies are in progress on the strength characteristics of commercial adhesives at cryogenic temperatures from -100° to -423° F (refs. 1 to 3). If the liner conforms to or is attached to the inside tank wall, however, it will be backed up by the fiber-glass shell at all times. Therefore, high strength in the adhesive joint, although desirable, is not the primary consideration. Since severe stresses are caused by the difference in thermal coefficient of linear expansion between adhesive and adherend when subjected to cryogenic temperatures, microscopic cracks can result that allow hydrogen to escape through the bonded joint. Thus, sealability becomes an important factor. At liquid-hydrogen temperature, however, data covering this characteristic of adhesives are lacking.

As part of the general study on evaluation of the filament-wound-tank concept, a preliminary experimental study was conducted at Lewis on the sealability of a limited number of commercially available adhesives. In this study, emphasis was placed on the ability of the adhesive to provide a hermetical seal in the presence of liquid and gaseous hydrogen. The adhesive-joint test specimens were fabricated from thin films that are probable candidate materials for liners. Lap joints were used with an adhesive bond line width of about 1/2 inch. The test specimens were designed and tested in a manner that would subject the adhesive bond line to a pressure difference of about 20 pounds per square inch but not to any mechanical stresses or loads.

The adhesives tested included epoxy-polyamines, nylon-filled epoxies, urethanes, polyesters, and rubber-based adhesives. Some of the adhesives were recommended by the manufacturer for use at very low temperatures, while others were not specifically designed or recommended for such use.

MATERIALS AND FABRICATION FOR TEST SPECIMENS

Adhesive Materials

A technical survey consisting of a review of literature, industrial inquiries, and personal contacts with individuals active in the cryogenic adhesive field was made to select the adhesives for the study. The survey showed that the adhesive industry has produced an extremely wide variety of adhesives with different properties and characteristics. Furthermore, almost an unlimited number of adhesives with different physical properties could be produced by slight changes in formulation or curing conditions. For most adhesives, data on properties were limited to bond-strength characteristics, and these were generally for a limited temperature range. Information on sealability and permeability was seriously lacking, even at room temperature. Enough information was available, however, to indicate the types and formulations of adhesives that might have good sealability characteristics at cryogenic temperatures.

The types of adhesives studied included epoxies, for their ability to be cured at low temperatures and bonding pressures; nylon-filled epoxies, for their superior strength at low temperatures; polyesters, because continuous pressure on the bond line is not required during curing; and rubber-based adhesives, for their room-temperature curing requirements.

The adhesives tested were all commercially available. The brand name, the source, and the type, when available, are listed in table I. In general, in the preparation of the test specimens, the adhesives were applied and cured as specified by the manufacturer. Near the end of the study, however, some test specimens were fabricated by using the more promising high-temperature-cure adhesives but were cured at room temperature. The curing temperatures and times are also indicated in table I.

Adherend Materials

Since the objective of the study was to evaluate the sealability of adhesives for use in fabricating lightweight liners for filament-wound cryogenic tanks, it was deemed necessary to test the adhesives with possible liner materials. Metallic foils and plastic films were used early in the study to fabricate adhesive test specimens, but leakage through these materials made evaluation of the adhesives difficult. Thus, these materials were abandoned in favor of a laminated material. This laminated material consisted of thin sheets of aluminum foil and Mylar (polyester film) bonded together. The laminated foil-film composite is available in either 2- or 3-ply construction. In the 3-ply or sandwich type, either material may occupy the central position. The binder used in the laminating process is a proprietary neoprene-base type formulated specifically for laminating metallic foil to Mylar film. In the lamination process, the binder

thickness is kept to a minimum to prevent delamination at low temperatures. Mylar is used with aluminum foil because of its superior strength and because the thermal expansion of Mylar (8.3×10^{-6} in./in. ($^{\circ}\text{F}$)) is about the same as that of aluminum (7.3×10^{-6} in./in. ($^{\circ}\text{F}$)). These values of coefficient of thermal expansion are overall average values from room temperature (68°F) to liquid-nitrogen temperature (-320°F). This similarity of coefficient of thermal expansion tends to retard delamination during temperature change.

For the adhesive tests reported herein, 3-ply laminated materials were used; an aluminum-Mylar-aluminum laminate, hereinafter called AMA, consisting of 0.001-inch-thick Mylar between foils of aluminum each 0.00035-inch-thick, and a Mylar-aluminum-Mylar laminate, hereinafter called MAM, consisting of a 0.00075-inch-thick aluminum foil between two films of Mylar each 0.001 inch thick.

Specimen Configuration

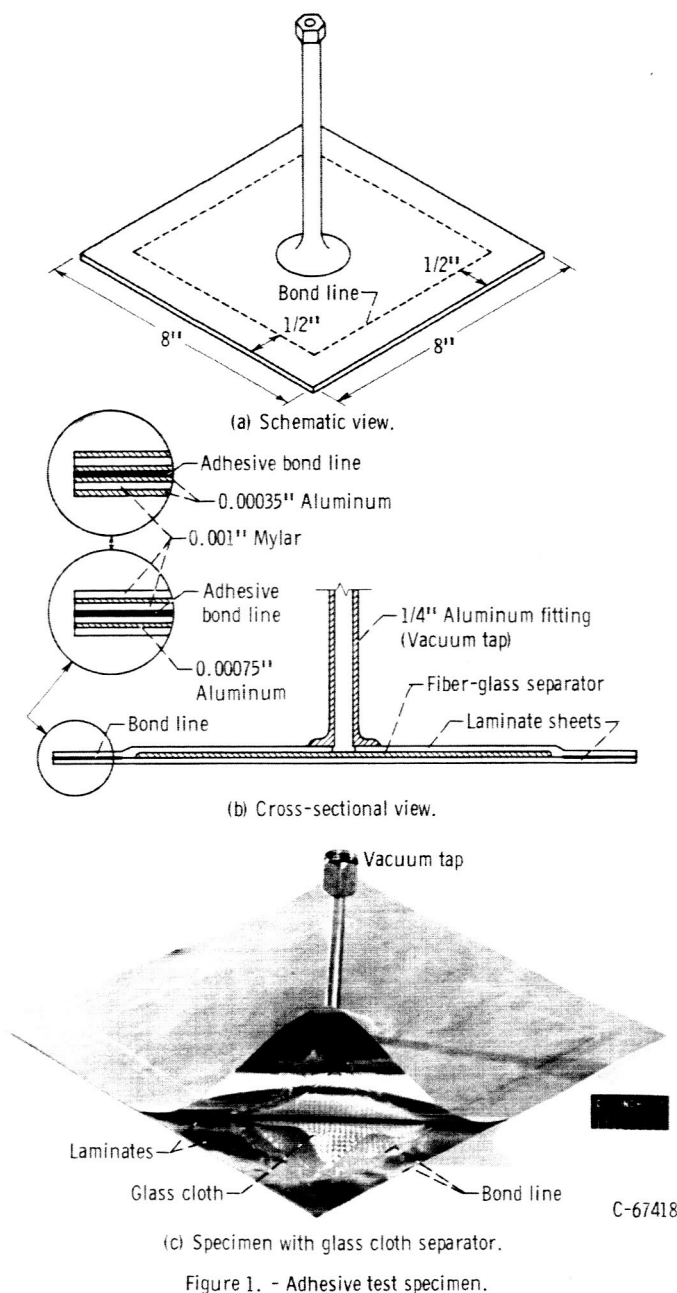
Inasmuch as the test objective was to determine the sealability of adhesives for making liners for filament-wound cryogenic tanks from thin laminated materials, several physical factors had to be considered in the design of the test specimen:

- (1) The adhesive joint has to form a part of an enclosed space.
- (2) The length of the adhesive joint should be as long as practical to make test results meaningful.
- (3) Since the thin films would require lap-type joints, the joint width in the test specimens should be typical of those required in fabrication of a liner.
- (4) The adhesive line thickness should be a minimum and uniform.
- (5) Tensile shear and peel loads on the adhesive should be a minimum when the specimen is under test, since strength of adhesive is secondary in this application.

The test-specimen configuration to meet these requirements consisted of two 8-inch-square pieces of laminate bonded together around their perimeter with the test adhesive, as shown in figures 1(a) and (b). The test adhesives were applied to a strip 1/2 inch wide. Inside the bond line, the two laminates were separated by a square piece (7 by 7 in.) of fiber-glass cloth 1/64 inch thick, as shown in figure 1(c). The cloth served as a separator to facilitate in the evacuation of the space between the laminates through the 1/4-inch-diameter aluminum nipple bonded in most cases with the test adhesive to the center of one side of the flat specimen.

Specimen Fabrication

The test-specimen-fabrication technique was standardized as much as possible with-



in the limits imposed by the individual adhesives and laminates. The technique evolved from preliminary experiments and consultations with manufacturers of adhesives and laminates. In the early phase of the study, test specimens were fabricated by several industrial companies as well as in-house at Lewis. Techniques and materials used in fabricating these specimens varied widely as did the test results. It became obvious that if a meaningful evaluation of the sealability of adhesives was to be obtained, the fabrication technique had to be standardized as much as possible. Thus, most of the test specimens for which results are presented herein were fabricated in-house by one individual. The principal fabrication steps are discussed in the following sections.

Surface preparation. - Preparation of the surfaces to be bonded together was necessary. Various methods were tried including sand-blasting. Two methods were selected, one for each of the two different laminates. For the AMA laminate (aluminum to aluminum bond) the surfaces were treated with a chemical compound designated as EX-13727-6 (refs. 4 and 5) and marketed under the trade name Chem-Lok. The Chem-Lok was brushed on the laminate and allowed to dry, after which it was washed off with water.

Surface preparation of the MAM laminate (Mylar to Mylar bond) consisted of a surface treatment using methylethyl ketone (MEK). The surfaces to be bonded were wiped with a clean cloth saturated with methylethyl ketone and then allowed to dry.

Assembly and curing. - The adhesives were applied to the bond areas generally in accordance with the manufacturer's recommendations. After the adhesive was applied

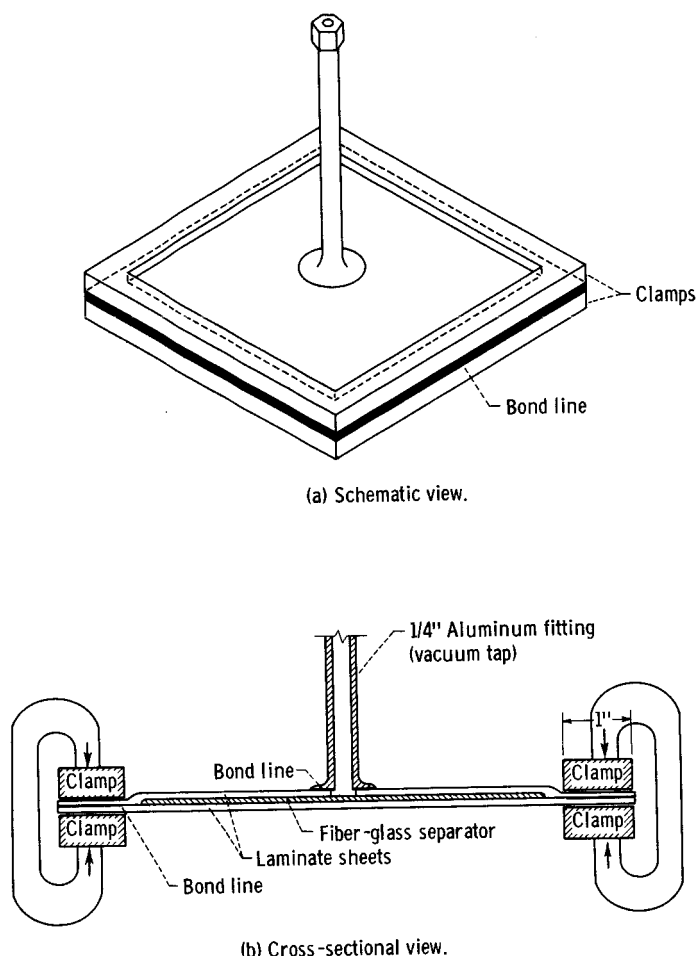
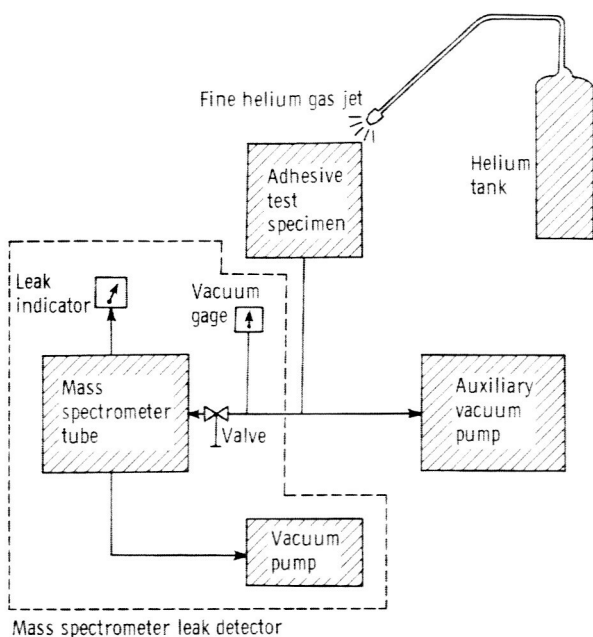


Figure 2. - Clamping arrangement for adhesive test specimen.

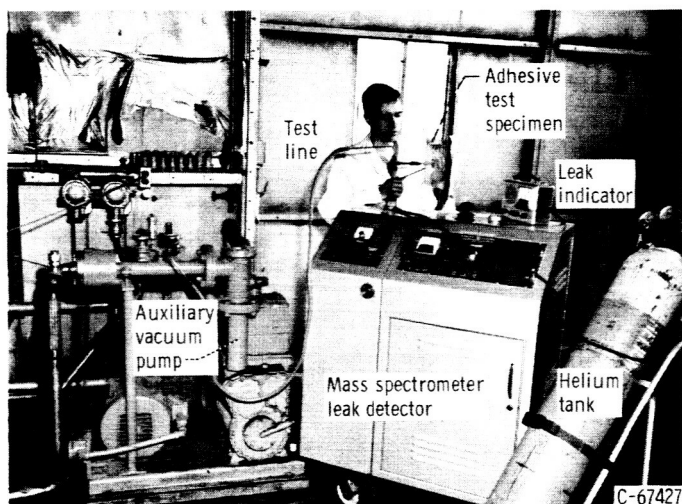
to the laminate bond area and the base of the vacuum tap, the glass cloth was put in place, the test specimen was assembled, and the bond areas subjected to pressure. The amount of pressure required for the various adhesives was not generally specified by the manufacturer. Two methods were tried to produce pressure on the adhesive joints; the vacuum-bag technique and mechanical clamping. The vacuum-bag technique was employed first because it would probably be employed for fabricating a three-dimensional liner for a filament-wound tank. Test results on specimens prepared by the vacuum-bag technique were more erratic than those made by the clamping method. Thus, the vacuum-bag method was discarded in favor of the simpler clamping method shown in figure 2. The amount of pressure applied to the bond line was not measured but was sufficient to squeeze out excess adhesive thus producing a thin, uniform adhesive layer.

Inspection of the specimens after the test showed that the applied pressure produced an adhesive area that varied in width from 1/2 inch to 1 inch, the clamp width (see fig. 2(b)). A few of the test adhesives did not require continuous pressure during curing, but a hot iron was used (as noted in table I under Curing). With a few exceptions, the adhesives used to bond the laminates were also used to bond the vacuum tap to the specimen. The exceptions, noted in table I, were some of the cases where the bond was between aluminum and Mylar. Pressure was applied to the adhesive on the vacuum tap by weights.

After the test specimens were assembled and clamped together, the adhesive was cured, in most cases, according to manufacturers' recommendations. Curing was done in an oven at temperatures from 70° to 320° F and times for 1 hour to 1 week. For some room-temperature cured adhesives, the time before test was a month, but they were cured for at least a week in a clamp. Many manufacturers recommended a range of curing temperatures and times. Increasing the temperature shortened the curing time



(a) Schematic diagram.



(b) Overall view.

Figure 3. - Test apparatus for adhesive-specimen room-temperature leak check.

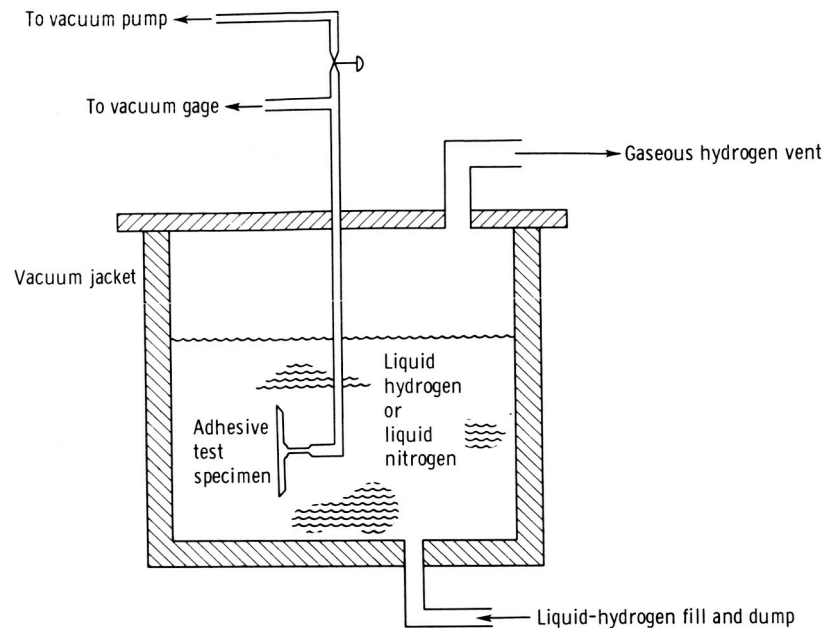
Room-Temperature Leak Check

The room-temperature leak-check apparatus is shown schematically in figure 3(a), and a physical layout is given in figure 3(b). A helium-mass-spectrometer leak detector with its associated vacuum pump is connected in parallel with an auxiliary vacuum pump to the adhesive test specimen. The auxiliary vacuum pump was used to evacuate the test specimen to a pressure of 100 microns of mercury or less. The vacuum was usually reached in about 3 minutes if the sample did not leak. Inability to achieve this vacuum was assumed to be caused by a leak. The leak was located by opening the valve to

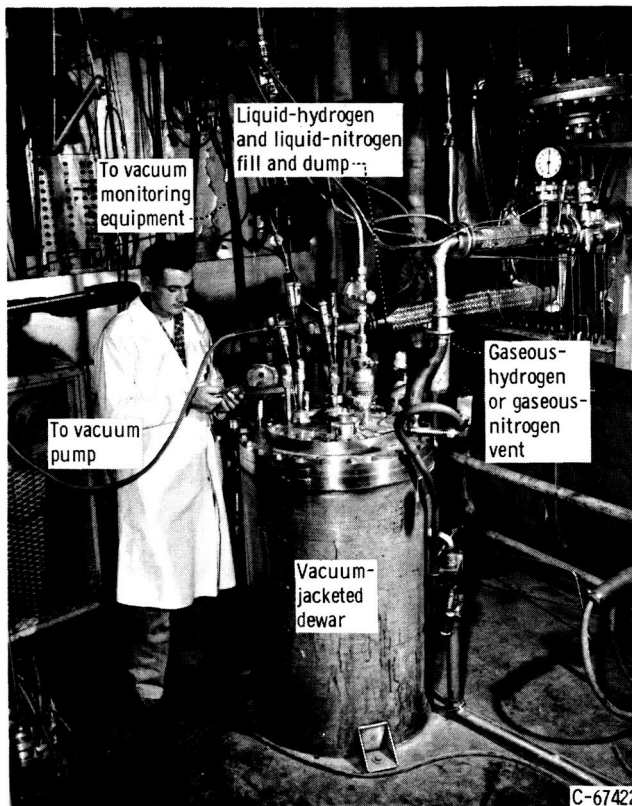
and generally produced a better bond. A few test specimens were made by using extremes in time and temperature to determine the effects on bond sealability. At the high curing temperatures, there is a possibility that the physical properties of the Mylar film were altered, but these properties were not evaluated in this study. The curing times, temperatures, and methods of applying pressure for each specimen are shown in table I.

TEST APPARATUS AND METHOD

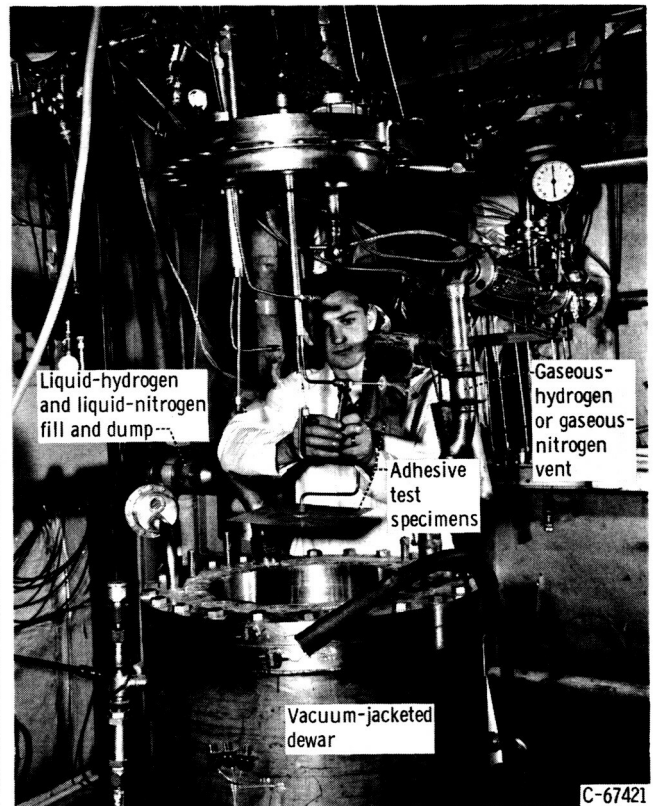
Evaluation of the sealability of the adhesive was based on the ability to evacuate and maintain a vacuum inside the flat test specimens. Since any hole through the laminate or adhesive would preclude the attainment of a vacuum, a test method was devised that would first indicate the presence of a hole and second locate the hole. Different test apparatus were required for room temperature and cryogenic temperatures.



(a) Schematic diagram.



(b) Overall view.



(c) Installation of test specimens.

Figure 4. - Test apparatus for adhesive-specimen cryogenic leak check.

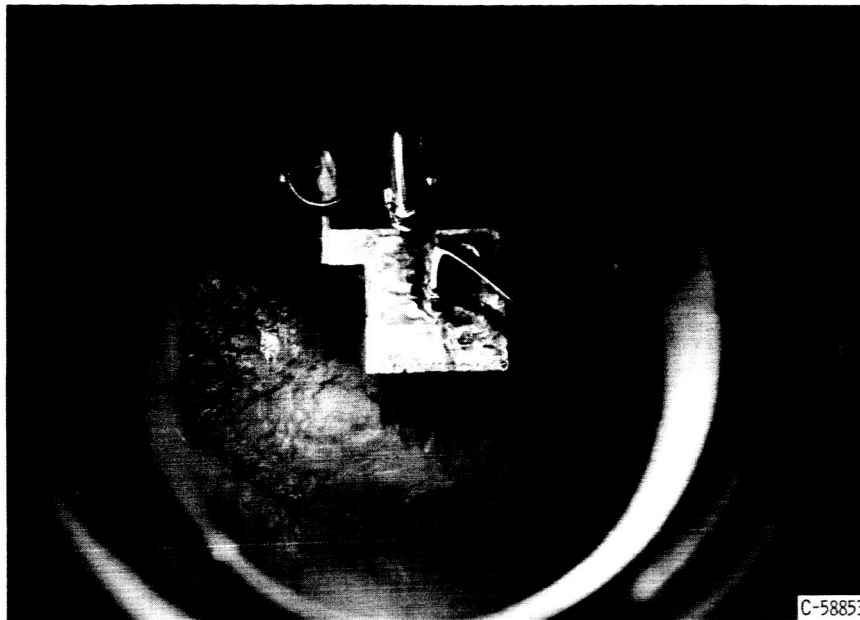


Figure 5. - Adhesive specimen submerged in liquid hydrogen.

the leak detector and surveying the test specimen with a fine jet of helium gas. Approximate location of hole was indicated by a maximum output signal from the leak-detector indicator.

Cryogenic-Temperature Leak Check

The cryogenic-temperature leak-check apparatus is shown schematically in figure 4(a), and the overall physical layout is shown in figures 4(b) and (c). The apparatus consisted of a vacuum-jacketed Dewar, a vacuum pump, and a vacuum monitoring system. The plumbing system of the Dewar allowed either liquid nitrogen or hydrogen to be used. Two test specimens could be tested simultaneously in the apparatus.

The test specimens were installed in the Dewar, and it was evacuated for a period of 4 hours at room temperature to reduce the effect of outgassing on the tests. Then the test specimen and vacuum-monitoring system were isolated by a valve from the vacuum pump for approximately 2 hours to observe any change in vacuum. The pressure usually stabilized at about 10 microns or less if no leaks were present. Then the Dewar was filled with either liquid nitrogen or liquid hydrogen until the test specimen was covered, as shown in figure 5. Pressure in the Dewar was maintained at about 5 pounds per square inch gage during the tests. The test specimen vacuum was monitored continuously. Cryopumping usually produced a decrease in pressure, if no leaks were present. After 15 minutes, the liquid was transferred from the Dewar, and the test specimen was warmed to room temperature by a flow of warm helium at 5 pounds per square inch gage through the Dewar. If no leaks were detected, cold shocking was repeated four times, once with liquid nitrogen and three times with liquid hydrogen.

Test Procedure

The complete chronological test procedure used to evaluate the sealability of the adhesives consisted of the following steps:

(A) An ambient-temperature leak check is made with a helium-mass-spectrometer leak-detector setup.

(B) A cryogenic-temperature shock is made by using liquid nitrogen in a Dewar setup.

(C) An ambient-temperature leak check is made with the leak-detector setup (same as step (A)).

(D-1) A liquid-hydrogen cold shock and a leak check in the Dewar setup are made.

(D-2) The Dewar is emptied, the specimen is warmed, and step (D-1) is repeated.

(D-3) Step (D-2) is repeated.

(E) An ambient-temperature leak check is made with the leak-detector setup (same as step (A)).

The test specimen vacuum was monitored during all phases of the cryogenic tests. Loss of vacuum at any time was considered a leak and is indicated in table I by the appropriate step letter.

RESULTS AND DISCUSSION

The sealability of 15 different commercially available adhesive formulations was tested as described in the section titled Test Procedure. In general, eight test specimens of each adhesive were tested, four bonding aluminum to aluminum surfaces (AMA laminates) and four bonding Mylar to Mylar surfaces (MAM laminates). For some adhesives, test specimens were not fabricated because of the limited scope of the investigation, and in some cases specimens failed for reasons other than adhesive bond-line leaks. The results are summarized in table I.

In general, the most satisfactory adhesive system for sealing aluminum to aluminum, Mylar to Mylar, and aluminum to Mylar (vacuum tap to MAM) are the epoxies and nylon-filled epoxies with an overall specimen failure rate of less than 8 percent. The overall specimen failure rate for urethane adhesive systems was 25 percent. The overall specimen failure rate for the polyester adhesive was 50 percent, and all the failures occurred in aluminum to aluminum bond. The rubber-based adhesive showed a 100-percent failure rate; half the specimens could not pass the first ambient-temperature tests, while the other half failed during the liquid-nitrogen cold-shock tests.

In addition to the adhesives listed in table I, another adhesive combination was tested on special test specimens. In order to find a suitable adhesive system for bonding

the aluminum vacuum tap to MAM, several test specimens were fabricated by using aluminum foil and MAM film, bonded together with DER 334 (20 percent) an epoxy resin made by Dow-Corning and Versamid 140 (80 percent) a polyamide made by General Mills. Tests of these specimens were very favorable. This adhesive combination was used to bond the vacuum tap on MAM specimens for polyester adhesives (specimens 14 and 15, table I).

During the course of the investigation, several adhesive tapes were used to make test specimens but with unfavorable results. It was also found that, for any of the adhesives, considerable care had to be exercised in the fabrication of the specimens. Excess resin had to be squeezed from the bond line, and foreign matter (dust) had to be kept out of the adhesive.

CONCLUDING REMARKS

All the adhesives tested are commercially available. Although some of the adhesives were recommended by the manufacturer for use at very low temperatures, others were not specifically designed for such use. Therefore, the fact that one adhesive produces a better sealed bond than another at cryogenic temperatures should not reflect on their value as bonding agents for other materials and temperature conditions.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 26, 1964.

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TABLE I. - SPECIMEN FABRICATION AND ADHESIVE SEALABILITY TEST RESULTS

Adhesive					Specimen fabrication				Specimen test results			
Specimen	Brand name	Manufacturer	Type	Composition, weight percent	Adher- end lami- nate	Curing			Number tested	Number failed	Test step of failure (b)	Remarks
						Time, hr	Temperature, °F	Pressure method				
1	7343/7139	Narmco	Urethane Moca	90 10	(a) AMA MAM	3.25 3.25	200 200	Clamped Clamped	4 4	1 1	D-1 D-2	Leak in bond line Leak in bond line
2	3135/7111	Narmco	Epoxy Polyamine	50 50	AMA MAM	0.75 .75	200 200	Clamped Clamped	4 3	0 0		
3	3170/7133	Narmco	Nylon-filled epoxy Nylon-filled polyamine	50 50	AMA MAM AMA MAM	0.5 .5 >100 >100	200 200 70 70	Clamped Clamped Clamped Clamped	4 4 4 4	1 0 1 0	D-3 A	Small leak unlocated; cold shocked six times Leaks at bond line and stem base
4	X-292	Narmco	Epoxy Methane diamine	88 12	AMA MAM AMA MAM	2.0 2.0 >100 >100	250 250 70 70	Clamped Clamped Clamped Clamped	4 4 4 3	0 0 0 0		Not fabricated
5	815/Epon T-1	Shell	Epoxy Polyamide	80 20	AMA MAM	1.0 1.0	250 250	Clamped Clamped	4 4	1 0	D-1	Undetermined leak Adhesive weak in peel strength at room temperature
6	Epon 828 Versamid 125	Shell General Mills	Epoxy Polyamide	65 35	AMA MAM AMA MAM	1.0 2.0 --- >100	150 150 --- 70	Clamped Clamped ----- Clamped	3 4 4 3	0 1 1 0	A	Leak in bond line Not fabricated
7	Epon 830 Versamid 125	Shell General Mills	Epoxy Polyamide	65 35	AMA MAM	1.0 1.0	150 250	Clamped Clamped	4 4	0 0		
8	EC 2216 B/A	Minnesota Mining and Manufacturing	Epoxy Modified amine	33 67	AMA MAM AMA MAM	1.0 1.0 >100 >100	150 150 70 70	Clamped Clamped Clamped Clamped	3 4 1 3	0 1 0 0	D-1	Leak in bond line
9	Aero-Bond 2010	Adhesive Engineering	Epoxy Polyamine	50 50	AMA MAM AMA MAM	0.5 .5 >100 >100	200 200 70 70	Clamped Clamped Clamped Clamped	4 4 4 1	0 0 0 1	A	Leak in bond line
10	DER 334 DER 20	Dow Corning	Epoxy Epoxy cure	90 10	AMA MAM	1.0 1.0	150 150	Clamped Clamped	3 4	1 0	D-2	Undetermined leak; adhesive weak in peel
11	Contact Adhesive CA 25	Miracle Adhesive	Rubber base	--	AMA MAM	>100 >100	70 70	Clamped Clamped	3 3	3 3	A A	All specimens leak at bond line at room temperature
12	Plibond	Goodyear Tire & Rubber	Rubber base	--	AMA MAM	>100 >100	70 70	Clamped Clamped	4 4	4 4	B B	
13	Topollic	Goodyear Tire & Rubber	Urethane- prepolymer polyester	--	AMA MAM	>100 >100	70 70	Clamped	1	0		
14	Vitel PE 207	Goodyear Tire & Rubber	Polyester	--	AMA MAM	Brush coat; dry 2 hr at 150° F; heat seal with 275° F iron			4	4	A	Gross leaks at bond line and stem seal Stem bond, DER 334 and Versamid 140; 8 hr at 70° F; clamped
15	46971	Dupont	Polyester	--	AMA MAM	Brush coat; dry 8 hr at 70° F; heat seal with 360° F iron			4	4	A	Gross leaks at bond line and stem seal Stem bond, DER 334 and Versamid 140; 8 hr at 70° F; clamped

aAMA, aluminum-Mylar-aluminum laminate; MAM, Mylar-aluminum-Mylar laminate.

bSee Test Procedure p. 10.